

FIRST PRINCIPLE INVESTIGATIONS OF HYDROGEN ADSORPTION IN METAL ORGANIC FRAMEWORK-5

by

MUHAMMAD HAFIZ BIN HUSSIM

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^a Yildirim et. al.

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LIST OF ABBREVIATIONS

BDC	1,4-Benzenedicarboxylate
BLYP	Becke, Lee, Yang and Par
BSSE	Basis set superposition Error
CBS	Complete-basis-set
CP	Counterpoise
CSD	Cambridge Structural Database
DFT	Density Functional Theory
DOE	U. S. Department of Energy
GCMC	Grand Canonical Monte Carlo
GGA	Generalized Gradient Approximation
HCTH	Hamprecht, Cohen, Tozer and Handy
HF	Hartree-Fock
H-K	Hohenberg-Kohn Theorem
HOMO	Highest Occupied Molecular Orbital
INS	Inelastic Neutron Scattering
IRMOF	Isorecticular Metal Organic Frameworks
LDA	Local Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
MOF	Metal Organic Frameworks
MP-n	n-Order Moller-Plesset
PBE	Perdew, Burke and Ernzerhof
PW	Perdew and Wang
SBU	Secondary building unit
STO	Slater type orbital

XRD

X-Ray Diffraction

LIST OF SYMBOLS

α	Binding site alpha
β	Binding site beta
γ	Binding site gamma
δ	Binding site delta
C_α	Center atom for binding site α
C_β	Center atom for binding site β
C_γ	Center atom for binding site γ
C_δ	Center atom for binding site δ

**PENYIASATAN PRINSIP PERTAMA PENJERAPAN HIDROGEN DI
DALAM KERANGKA LOGAM ORGANIK -5**

ABSTRAK

Kajian perkomputeran orbit-molekul telah dijalankan untuk mencari tenaga dan kedudukan ikatan bagi penjerapan molekul hidrogen di dalam Kerangka Logam Organik – 5 (MOF – 5). Lima model molekul bagi MOF-5 (model molekul M1 hingga M5) telah dikaji untuk mencari kesan koordinasi sambungan kekisi 1,4-*Benzenedicarboxylate* (BDC) dan skim penamatan kekisi tergantung terhadap tenaga dan kedudukan ikatan dalam penjerapan molekul hidrogen. Kajian peringkat awal telah dijalankan untuk menilai kecekapan kaedah Teori Fungsi Ketumpatan untuk mencari kedudukan ikatan dan tenaga ikatan bagi penjerapan molekul hydrogen pada molekul BDCLi_2 . Kaedah ini dengan fungsian HCTH dan set basis 6-31G(d) telah dipilih sebagai kaedah bagi semua pengiraan tenaga ikatan dan kedudukan ikatan di empat tapak ikatan α , β , γ , dan δ dengan orientasi menegak dan selari. Basis set tahap tinggi telah didapati dapat memberikan keputusan dengan ketepatan tinggi tetapi dengan keperluan komputeran yang tinggi. Didapati bahawa koordinasi sambungan kekisi dan skim penamatan kekisi tergantung boleh mempengaruhi tenaga ikatan bagi molekul hidrogen terhadap tapak β dan γ pada kesemua model molekul. Model molekul M5 telah diuji bagi penjerapan sebilangan molekul hidrogen dengan menggunakan kaedah pengoptimuman separa. Penjerapan berbilang molekul hidrogen telah didapati lebih digemari berbanding dengan penjerapan satu molekul

hidrogen untuk semua tapak penjerapan kecuali tapak β . Oleh itu penjerapan berbilang molekul hidrogen perlu dipertimbangkan bagi pengiraan kedudukan ikatan dan tenaga ikatan untuk model molekul MOF-5.

FIRST PRINCIPLE INVESTIGATIONS OF HYDROGEN ADSORPTION IN METAL ORGANIC FRAMEWORKS-5

ABSTRACT

Computational molecular-orbital study had been conducted to find the binding energy and binding position of Metal Organic Frameworks – 5 (MOF – 5) for hydrogen molecules adsorption. Five model molecules (model molecule M1 to M5) for MOF-5 were investigated to find the effects of the 1,4-*Benzenedicarboxylate* (BDC) linker coordination and dangling bonds terminator scheme on the binding energy and the binding position of the absorbed hydrogen. In the initial stage study, we had performed the calculations using the Density Functional Theory method to determine the binding position and binding energy of hydrogen molecule near the BDCLi_2 molecule. This method with HCTH functional at 6-31G(d) basis sets was chosen as the procedure for all calculations of binding energy and binding position of four binding sites namely the α , β , γ , and δ sites both in the perpendicular and parallel orientation of the hydrogen molecule. The higher order basis sets were found to provide more accurate results but with higher computational cost. It was found that the BDC linker coordination and dangling bonds terminator scheme do affect the binding energy of the hydrogen molecules at the β and γ sites of the MOF-5 model molecules. Model molecule M5 was tested for multiple hydrogen molecules adsorption using partial optimization method. It was found that multiple hydrogen molecules adsorption is more favourable as compared to the single hydrogen

molecule adsorption at all binding sites except for the binding site β . Thus multiple hydrogen adsorptions should be considered for the binding energy and binding site calculations for the MOF-5 model molecule.

Chapter 1

INTRODUCTION

1.1 Metal Organic Frameworks

Metal Organic Frameworks (MOFs) have been proposed as a possible solution to the hydrogen storage problem. With the focus on finding alternative and environmental friendly energy resources, hydrogen becomes a prime candidate of the future energy. One of the stumbling block in using hydrogen as a future energy resources is its storage. Hydrogen storage is one of the important topics in addressing hydrogen economy. The method of storing hydrogen for subsequent use is important especially for onboard hydrogen storage in hydrogen fuelled vehicles in the future. In 2010, the U.S. Department of Energy (DOE) released a target of gravimetric and volumetric hydrogen storage capacity of 6 wt% and 45 g H₂/L respectively for the year 2010 and 9 wt% and 81 g H₂/L for the year 2015 [1]. Gravimetric capacity is defined as the percent of hydrogen weight as compared to the complete storage system weight. Volumetric capacity is defined as the weight of hydrogen gas divided by the total volume of storage.

Currently there are two available methods of storing hydrogen which are using liquid hydrogen or storing it in a compressed form. Liquid state hydrogen or slush hydrogen that has been used in space shuttle requires cryogenic storage as hydrogen boils around 20 K. Hence energy required for maintaining this cryogenic state is immense and imposes large energy loss. The tank also needs good insulation to prevent hydrogen boil off. However liquid hydrogen is a proven technology and has exceeds 2015 DOE target for gravimetric and volumetric for hydrogen storage.

Meanwhile hydrogen in compressed form is a storage option where the hydrogen is still in gaseous state and kept under pressure. Compressed hydrogen at 350 bar and 700 bar is currently being used in prototype hydrogen vehicles [2]. Higher pressure will provide higher energy density. Higher pressure will also require substantial amount of energy for the compression of the gas. A large hydrogen tank will be too heavy to contain the high pressure.

Current research trends in hydrogen storage are in chemisorption and physisorption of hydrogen into a substrate. Chemisorption involves chemical binding of hydrogen molecules into a substrate. Most metal hydrides bind with hydrogen very strongly. Lithium, aluminium and boron based compounds already show good prospect for hydrogen storage. Other types of chemisorption properties are also shown in molecules such as carbohydrates, ammonia, formic acid, phosphonium borate and imidazolium ionic liquid [3].

Meanwhile physisorption of hydrogen molecules into a substrate does not involve strong chemical binding to the substrate itself. Some molecules show good attraction to hydrogen for example carbon nanotubes, MOFs, clathrate hydrates and glass capillary. One notable type of MOF family known as MOF 177 could store hydrogen up to 7.0 wt% and 32 g H₂/L in gravimetric and volumetric respectively at 77K and 70 bar [4]. Physisorption of Hydrogen in MOF 177 has exceeded DOE volumetric target for 2010 and becomes a promising candidate for onboard hydrogen storage as compared to other technologies.

MOFs are crystalline inorganic-organic hybrid structures that contain metal cluster or secondary building unit (SBU) and organic ligands as linker. MOFs have very high number of pores and surface area which allow high hydrogen uptake. Due to the basic structure of MOFs, there are infinite combinations of SBUs and organic

linkers currently being studied to provide maximum hydrogen uptake. MOFs are crystalline compound that consists of metal ion coordinated to organic molecules to form a one, two or three dimensional structures. It can be tailored to specific applications by varying the cluster of metal ions and organic molecule or linkers. The number of potential MOFs is virtually limitless as changes in metal ions or secondary building blocks and the organic linkers will produce novel MOFs with distinct properties. The coordination of metal ion clusters and organic molecule linkers will create porous crystalline MOF with large voids and high surface area within the structure [5].

The concept of MOFs based on metal ionSBUs bridged to other organic ligands was well known since the late 1980s. However, the outstanding work performed by Yaghi on this class of crystalline materials, was responsible for the real breakthrough of MOFs [3]. They found that the use of carboxylate rigid organic ligands to aggregate metal-ions is ideal to form extended frameworks with structural stability and high porosity. Indeed, the strong metal-oxygen bond confers exceptional robustness to the framework which does not collapse even after the removal of the solvent molecules incorporated during its synthesis. The result is a crystalline ordered framework possessing low density and high specific surface area. The key to design MOFs is in the assembly of metal-carboxylate subunits as nodes of a framework and of organic linkers in the desired network topology [6]. An example is given by the structure of MOF-5 [7], which is the most studied of all metal organic framework due to its high specific surface area and to the simple and cheap starting material to produce. Figure 1.1 shows the crystal structure of MOF-5.

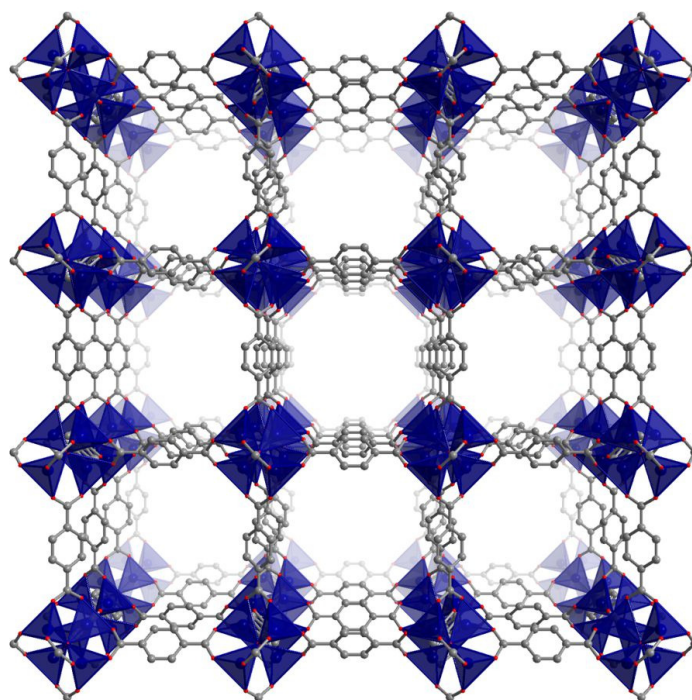


Figure 1.1. : MOF-5 crystal structure shows metal-carboxylate subunits as nodes of a framework (blue polyhedral) and of organic linkers (grey) [8].

The ability of MOFs to absorb hydrogen molecules and other light gases makes it a good candidate for efficient hydrogen storage. Other applications for MOFs are in other gas storage and separation. MOFs are also known to absorb other types of gases such as carbon dioxide, carbon monoxide, methane and oxygen. Gas separation can be performed using MOFs by allowing certain gas molecules to pass through by variation of pore sizes.

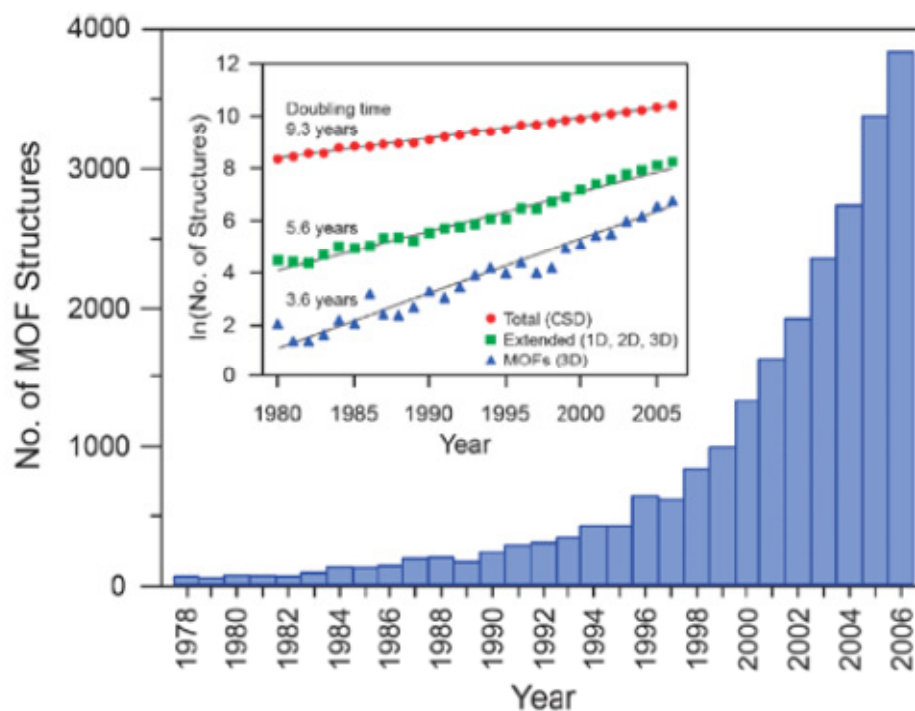


Figure 1.2 : Number of MOF structures reported in the Cambridge Structural Database (CSD) from 1978 to 2006. The bar graph illustrates the recent dramatic increase in the number of reports, while the inset shows the natural log of the number of structures as a function of time [9].

At present, there are several types of MOFs that exist in physical form and also in its prototypical form. A very large number of MOFs with various pore size, topology and functionality have been synthesized over the years. Figure 1.2 shows the number of MOFs structures reported in Cambridge Structural Database (CSD) from 1978 through 2006 [9]. The most successful and widely studied MOF is MOF-5 found by Yaghi group in 1999 [6]. MOF-5 is currently readily available in industrial-scale synthesised by BASF chemical company [10]. MOF-5 is also the first member of Isorecticular MOF or IRMOF which shares a common cubic crystal structure. The variation of organic linker to the same cubic crystal structure will produce other types of IRMOFs.

A wide variety of IRMOF structures are possible. The IRMOF materials have the same zinc oxide SBU as that of IRMOF-1. Other IRMOF materials have the linker molecules with additional functional groups on the aromatic rings, or multiple

aromatic rings. For the IRMOF crystals with long linker molecules, interpenetrating (catenated) structures are possible. For example IRMOF-11 is the catenated structure of IRMOF-12. Figure 1.3 shows various types of IRMOFs from IRMOF-1 to IRMOF-16 with different type of organic linkers and catenated structures.

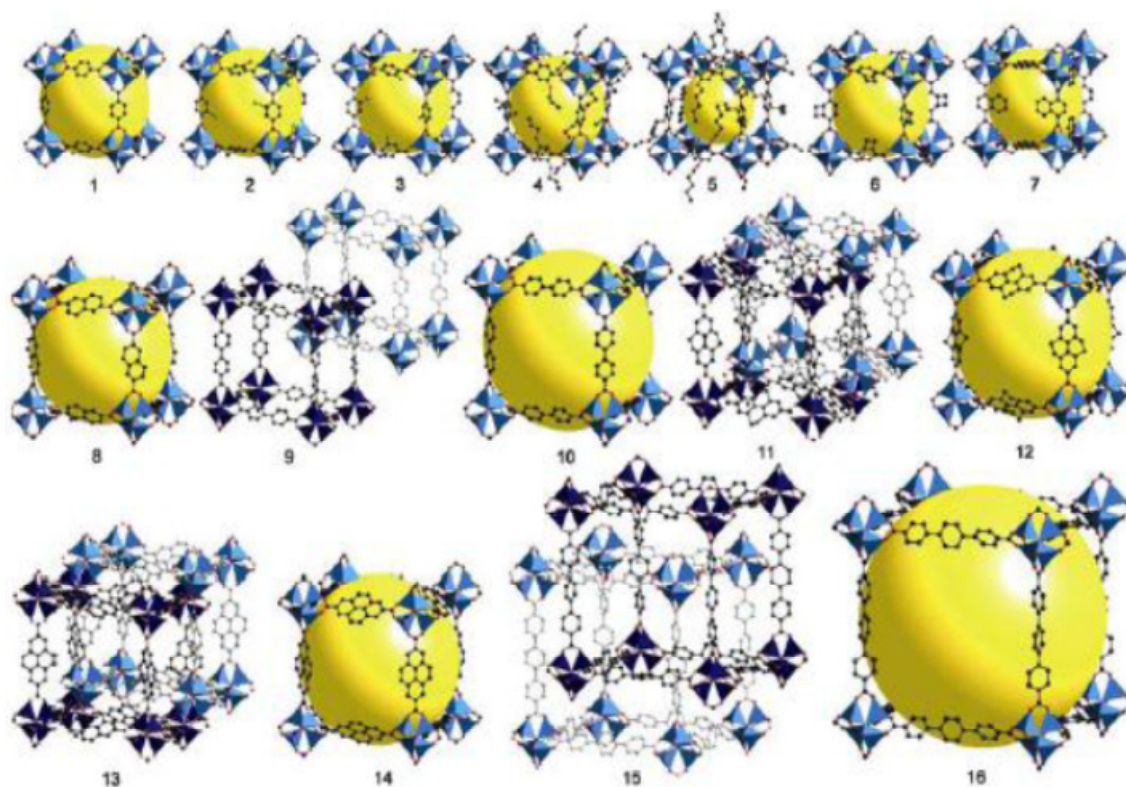


Figure 1.3 : Single crystal structure of IRMOF-n ($n = 1$ to 16). The large yellow spheres represent the largest empty space area that would fit in the cavities without touching the frameworks [11]

1.2 Computational studies on MOFs

Computational studies on MOFs started as soon as MOF-5 was discovered by Yaghi research group [6]. The main concern of this computational study is in finding the interaction of the hydrogen molecule with MOFs using theoretical approach such as ab initio and Density Functional Theory (DFT) calculations. Other computational studies on MOFs concerned on the bulk hydrogen adsorption in MOFs molecules

using Grand Canonical Monte Carlo (GCMC) simulations [12]. This computational study may simulate Hydrogen loading into MOFs. Figure 1.4 shows a single cell molecular structure of MOF-5 molecule with its chemical formula of $\text{Zn}_4\text{O}(\text{BDC})_3$ where BDC^{2-} is 1,4-Benzenedicarboxylate.

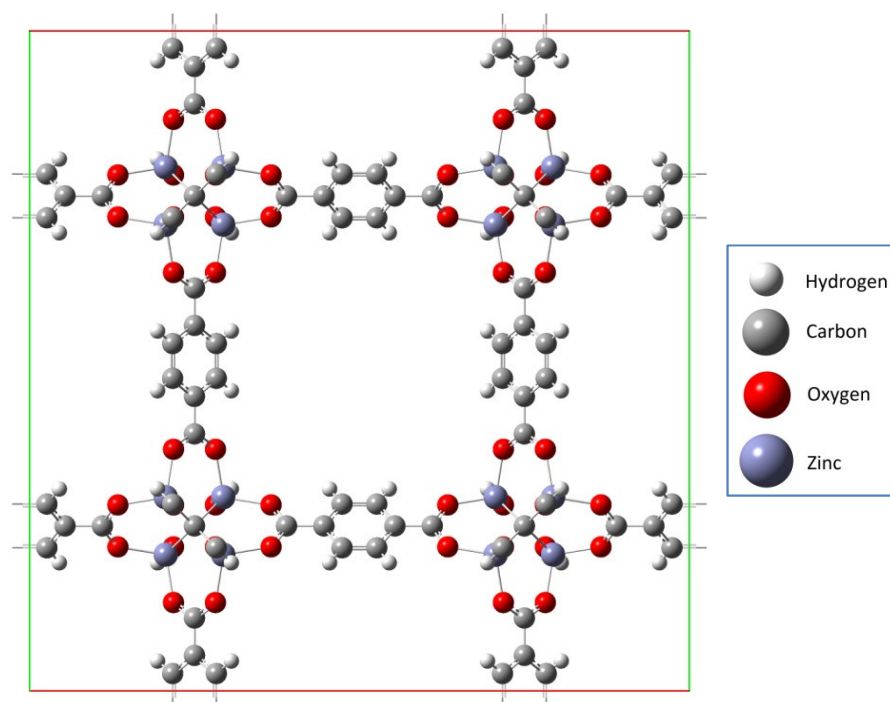


Figure 1.4 : Molecular structure of MOF-5.

After Yaghi group reported high hydrogen uptake in MOF-5 in 2003, Huber et al. almost promptly investigated hydrogen binding to MOFs using a theoretical approach in 2004 [13]. The focus of their study is on the interaction of hydrogen to organic linkers using Second Order Moller-Plesset (MP2) calculations. They indicated that the enlargement of the organic linker will increase the binding energy of Hydrogen. Other works by Segara et al. in the same year also proves that organic linker plays its part in hydrogen binding to MOFs as well as the metal cluster SBU in it [14]. Using MP2 ab initio method, they indicated that the zinc oxide cluster has higher hydrogen binding energy compared to the organic linker. In a later study in 2005 Segara et al. recalculated a more accurate hydrogen binding energy in MOF-5

and also calculated the hydrogen binding energies to other type of linkers which constructs other type of IRMOFs including IRMOF-1, IRMOF-3, IRMOF-6, IRMOF-8, IRMOF-12, IRMOF-14, IRMOF-18 and IRMOF-933 [15,16]. They found that the addition of NH_2 and CH_3 group to each linker will increase the hydrogen binding energy by up to 33%. There are many other ab initio studies in determining hydrogen binding energy in MOFs but they are limited to individual organic linker or metal cluster SBU in MOFs. These ab initio studies mainly focus on the effect of enhancements in organic linker or metal cluster SBU to increase the hydrogen binding energy for example by using novel organic linkers, other types of metal cluster SBU or by using metal decorated MOFs.

ab initio studies on MOFs are concentrated on small fragment of MOF-5 either by analyzing its zinc cluster SBU unit only or by using its 1,4-Benzenedicarboxylate (BDC) linker only. Segara et al. used BDC linker terminated by two lithium atoms at both ends to simulate the metal cluster near the corner of MOF-5 which is also known as BDCLi_2 (Figure 1.5) [16]. The lithium atoms at both ends of BDC molecule will simulate the SBU units at both ends of the linker. This model will minimize the number of atoms involved and therefore is suitable for ab initio calculation. Some researchers such as Lee et. al [17] and Kolmann et. al [18] further simplified this model by using benzene only to simulate the organic linker. This model can be adapted for other possible types of organic linker with MOFs such as boroxine, pyridine, pyridazine, triazole, furan and thiophene [19]. Ab initio study is also applicable by using SBU only terminated by six hydrogen atoms at all of its dangling bonds. This method has been studied by Fu et. al [20] to find the interaction energy and position of hydrogen near the SBU. Figure 1.5 shows the BDCLi_2 model molecule used to model BDC linkers exists in MOF-5 molecule. Figure 1.6 shows

the MOF-5 model that is built upon the SBU which consists of Zn_4O with no BDC linker terminated with hydrogen atoms.

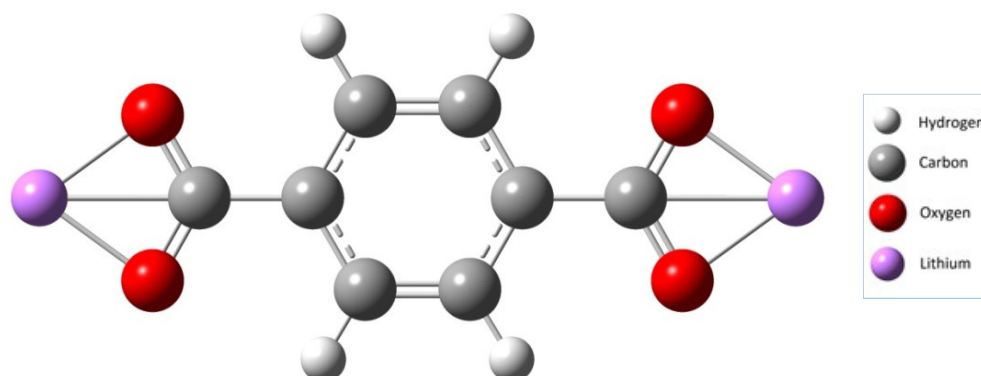


Figure 1.5 : BDCLi_2 linker only structure.

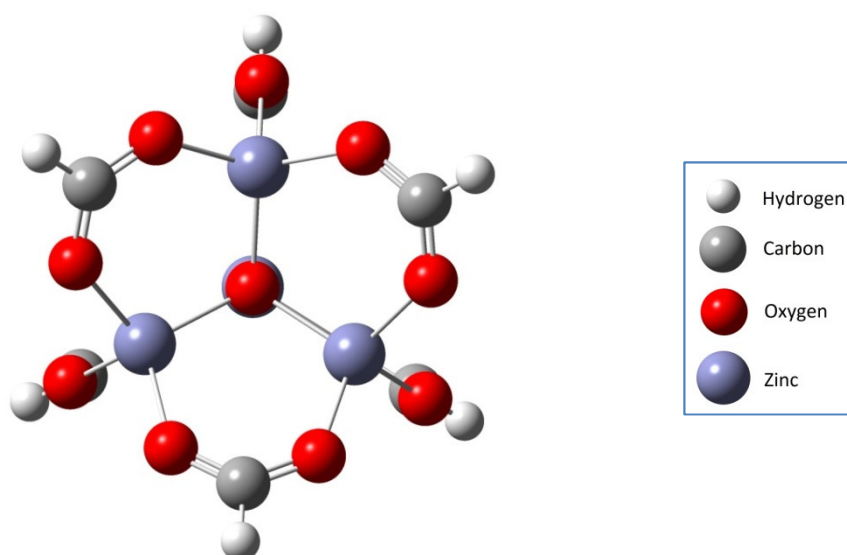


Figure 1.6 : Zn_4O connected to carboxylate group from BDC linker later known as Model M1.

To consider the full periodic crystal structure of MOFs, one needs to use DFT method because of its lower computational cost as compared to the ab initio method. Mulder et al. [21] and Mueller et. al [22] reported strongest hydrogen binding near SBU compared to its organic linker in MOF-5 using DFT technique. They were able to include partial structure of MOFs crystal with zinc cluster SBU connected to its organic linker. Since the interaction of hydrogen to MOFs is mainly the van der

Waals dispersion forces, ab initio method is the best option to calculate hydrogen interaction energy. However DFT method poorly predicts this type of interaction. With the advantage of DFT method in analyzing full periodicity of MOF and greater advantage in calculation time, it is able to provide good information on the hydrogen adsorption sites and binding energies which include the interaction with both metal ions SBU and its organic linkers.

Modelling the interaction between molecular hydrogen and MOF is a difficult task because the interaction may be caused by nonlocal electronic correlation. With large unit cell of MOF-5, calculating the whole periodic MOF-5 crystal structure is very expensive in term of time and computational cost. Therefore the task of selecting appropriate partial MOF-5 model suited for DFT calculation is important to accurately calculate the binding energy and binding position of hydrogen in MOF. Creating partial model of MOF-5 also involves the problem of terminating the dangling bonds. Functionals of DFT will also affect the outcome of the computation. These are some issues that should be considered prior to the calculation of binding energies and binding sites of molecular hydrogen near the MOF. There are several previous studies involved in using DFT to calculate hydrogen and other light gases binding energy and binding sites in MOF-5 [17-22]. Those studies did not apply the same level of theory in DFT calculation, the same partial model of MOF-5 and dangling bonds terminator scheme. This will affect the calculation of hydrogen binding energy and binding sites in MOFs. This thesis will evaluate and compare the available partial models of MOF-5 used by various researchers with different terminator schemes using DFT calculation.

Partial model of MOF-5 used to simulate the whole periodic crystal structure are basically divided into two distinct models proposed by a number of researchers.

The first model for MOF-5 molecule for DFT calculation was proposed by Lee et al. by using two zinc cluster SBUs connected by a single BDC linker [17]. This MOF-5 model molecule will create ten dangling bonds near the zinc cluster SBU unit. This kind of MOF-5 model was also adopted by other researchers such as Sillar et. al [23], Pianwanit et.al [26], Mu et. al [27] and Dixit et. al [28]. The dangling bonds are terminated either by using hydrogen or acetate groups. Figure 1.7 shows two zinc cluster SBUs connected by a single BDC linker terminated with hydrogen atoms. Figure 1.8 shows two zinc cluster SBUs connected by a single BDC linker terminated with acetate groups.

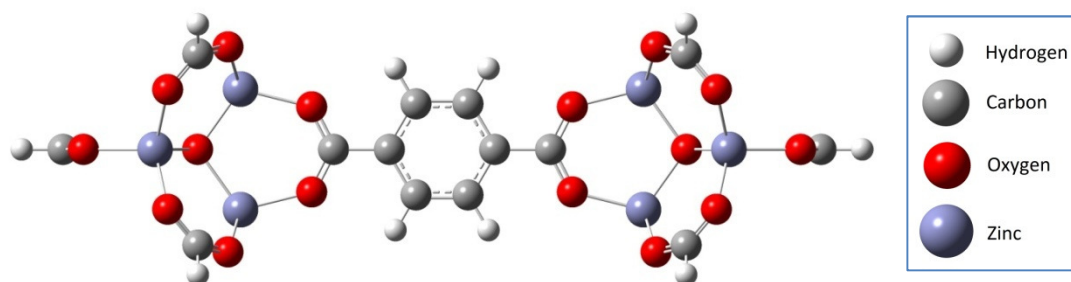


Figure 1.7 : Two zinc cluster SBUs connected by a single BDC linker terminated with hydrogen atoms later known as model M2.

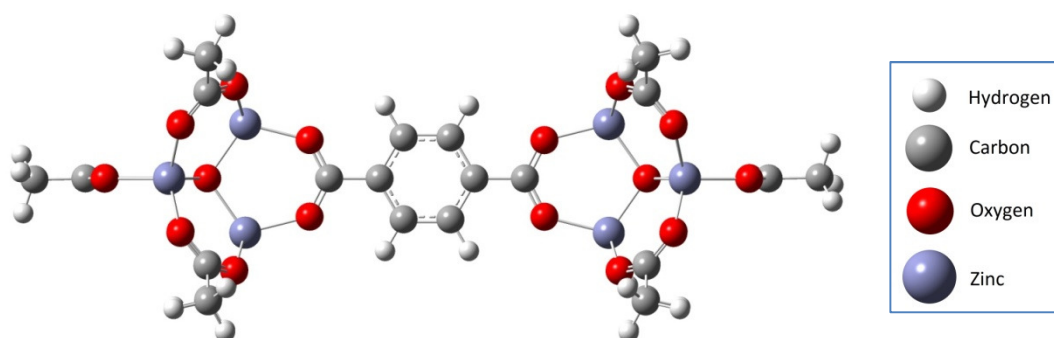


Figure 1.8 : Two zinc cluster SBUs connected by a single BDC linker terminated with acetate groups later known as model M3.

The other model proposed by Mueller et. al used single zinc cluster SBU connected by six BDC linkers [22]. This model creates six dangling bonds at the end

of the six BDC linkers. Other researchers that applied this kind of MOF-5 model are Sillar et. al, [23] Dubbledam et al. [24] and Klontzas et al [25]. All dangling bonds created by this model are terminated either by removing carboxylate group and replacing it with hydrogen atom, or terminating with lithium atom near the carboxylate group in the linker. Figure 1.9 shows an MOF-5 model molecule with a single zinc cluster SBU connected by six BDC linkers terminated with hydrogen atoms. Figure 1.10 shows other type of MOF-5 model molecules with a single zinc cluster SBU connected by six BDC linkers with its carboxylate groups terminated with lithium atoms.

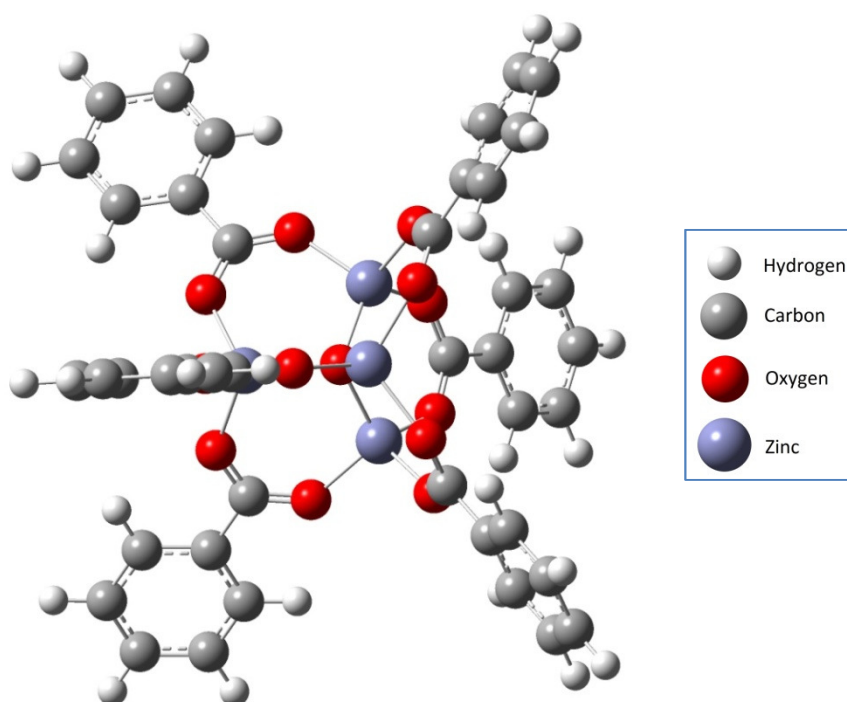


Figure 1.9 : Single zinc cluster SBU connected by six BDC linkers terminated with hydrogen atoms later known as model M4.

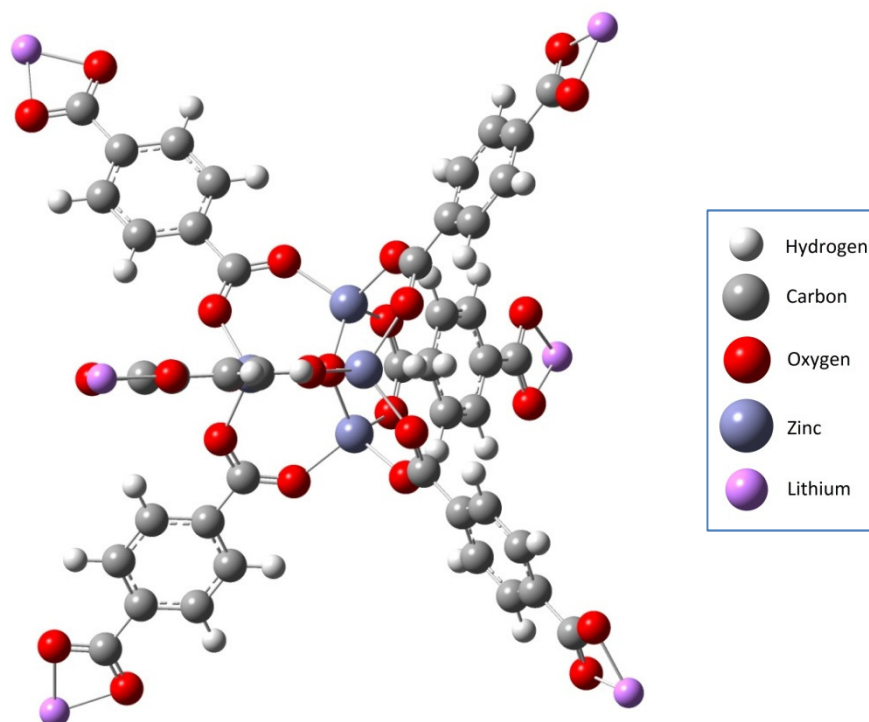


Figure 1.10 : Single zinc cluster SBU connected by six BDC linkers with carboxylate groups terminated with lithium atoms later known as model M5.

Even though all model molecules are capable of producing binding energies and binding sites for hydrogen molecules near MOF-5, it is important to determine the best method to show how the differences for each model molecules affect the outcome of the binding energies and binding positions of hydrogen molecule. The coordination of zinc clusters SBU and organic linkers might have some effect on the binding energies and binding position of hydrogen molecules near MOF-5 model. Furthermore the differences in the terminator regime will change the outcome on those binding energies and binding positions calculated from each model molecules.

The challenge in using computational method on MOF-5 molecule is to find the most suitable method to simulate hydrogen molecules binding. Modeling the interaction between hydrogen and MOF-5 is difficult because a significant portion of the interaction could be caused by non local electronic correlation. ab initio methods such as MP2 and other post Hartree-Fock methods accurately evaluate this type of

interaction but typically scale poorly with the model size making them computationally expensive. Studying only a part of the framework might produce bias results that are specific to adsorption site and overlook other important interactions between the framework and hydrogen molecule. To simulate hydrogen molecule binding near the MOF-5 molecule, DFT method is a good choice because it can consider a larger MOF-5 model molecule. Consequently the effect of both zinc cluster SBU unit and its BDC organic linker to the hydrogen molecule binding energies and binding positions will be well addressed using DFT method.

However the interaction between MOF-5 with hydrogen molecules is based on the weak van der Waals interaction. DFT method often fails to accurately calculate the weak interactions of electron correlation exist in van der Waals interaction. Some DFT functional such as PW91, PBE and HCTH are known to be able to model this kind of weak interaction.

Therefore it is important to find the most suitable DFT functional to represent the interaction between hydrogen molecules and MOF-5. The result for interaction energy between hydrogen molecules and MOF-5 should be close to the ab initio calculation at a comparable position. Furthermore, the type of MOF-5 model with its terminator atoms should represent the periodic structure of MOF-5 crystal structure. Therefore it is important to choose the right MOF-5 model for the right balance between accuracy and computational cost.

1.3 Scope of the Thesis

Development of technological applications based on nanoporous materials requires fundamental understanding of their properties at a microscopic level. With

ever growing computational power, molecular simulations are playing increasingly important role in the development of new materials. Simulations at the molecular scale can provide microscopic pictures that otherwise are experimentally inaccessible or difficult to obtain. In conjunction with experiment, fundamental insight gained from molecular simulations can assist the rational design of novel materials and products. In addition, this approach can be extended to hypothetical structures that are yet to be prepared in experiments. Because of the predictability of the synthesis routes to MOFs and the nearly infinite number of possible variations, molecular simulations are attractive for screening new MOFs before experimental synthesis and testing. The main goal of this thesis is to understand the adsorption phenomena of hydrogen in MOFs using molecular simulation techniques and subsequently provide a fast and reliable method for the screening and design of high-performance MOFs for important applications. The objectives of this research are;

1. To find the best technique of finding binding energy and binding position for BDCLi_2 model for subsequent use in MOF-5 models.
2. To determine the effects of different terminators on the geometrical parameters of MOF-5 models.
3. To determine the most suitable model to simulate MOF-5 molecule absorbing a single hydrogen molecule using energy profiling method.
4. To evaluate the binding sites and binding energies of multiple hydrogen molecules absorbed in MOF-5.

Five models of MOF-5 are considered in this thesis. These models are listed in Table1.1.

Table 1.1 : MOF-5 model molecules listed as model molecules M1 to M5 used in this study to represent different types of zinc cluster SBU and organic linker coordination and different terminator scheme.

Models	Description
M1	Single zinc cluster SBU terminated with hydrogen atoms. (Refer to Figure 1.6)
M2	Two zinc cluster SBUs connected with a BDC linker terminated with hydrogen atoms. (Refer to Figure 1.7)
M3	Two zinc cluster SBUs connected with a BDC linker terminated with acetate group. (Refer to Figure 1.8)
M4	Single zinc cluster SBU connected to six BDC linkers with carboxylate group replaced with hydrogen atom. (Refer to Figure 1.9)
M5	Single zinc cluster SBU connected to six BDC linkers terminated with lithium atom. (Refer to Figure 1.10)

From Table 1.1, model molecule M1 will serve as a control model with no organic linkers at all to find the effect of the number of organic linkers that exists in model molecule M2 through M5. Model molecule M2 and M3 is used to compare the model of MOF-5 molecule with two zinc cluster SBUs connected by a single BDC linker. All dangling bonds in model molecule M2 are terminated using hydrogen atoms while the dangling bonds in model molecule M3 is terminated by acetate terminator. Model molecule M4 and M5 represents an MOF-5 model that comprises single zinc cluster SBU connected by six BDC linkers. The dangling bonds at the end of each BDC linkers in model molecule M4 are terminated with hydrogen atoms while in model molecule M5 they are terminated using lithium atoms at the end of each carboxylate group.

1.4 Organization of the Thesis

The thesis is organized into six chapters, including the Introduction in Chapter 1 that discusses the development of MOFs and the background of computational approaches in previous studies. The description of the method employed in the thesis is discussed in Chapter 2. The results and discussions pertaining to the objectives mentioned in section 1.3 are discussed in Chapters 3 through 5. More specifically, Chapter 3 focuses on finding the best and reliable DFT method in locating the binding sites and binding energies of hydrogen molecule. The role of different MOF-5 models on the geometrical parameters of MOF-5 is discussed in Chapter 4. Furthermore Chapter 4 discusses the effects of different models on the binding sites and binding energies of hydrogen molecules. In Chapter 5, characterization of multiple hydrogen bindings using the best MOF-5 model molecule available is investigated using energy optimization technique. Finally, the concluding remarks and the recommendations for future studies are given in Chapter 6.

Chapter 2

METHODOLOGY

2.1 Computational Studies

Molecular modeling and simulation study are complementary to experimental and theoretical analysis and play a critical role in understanding, characterizing, and developing adsorption system for MOFs. For example, using simulation, the potential of proposed but unsynthesized candidate MOF structures can be screened without costly laboratory synthesis and adsorption measurements for underperforming materials. Furthermore, identification via simulation of structural features and chemistries to yield new MOFs that are well suited to particular conditions can justify the development of new generations of engineered MOFs specifically tailored for the desired application. Furthermore, simulation allows the study of phenomena that occur under conditions and at scales that are difficult to reproduce in a laboratory setting. Molecular modeling and simulation studies of MOFs are focused in finding the binding sites and binding energies near the MOFs structure.

Before attempting to find the binding energy and binding position of hydrogen in MOF-5 molecule, it is important to find the most suitable density functional theory (DFT) method that gives the result closest to highly accurate ab-initio method. Therefore comparing the result of DFT calculations with the ab initio method is crucial in deciding the most suitable DFT method with different types of functionals and basis sets.

2.2 Density Functional Theory

Schrödinger equation is a way to calculate the ground state energy of a collection of atoms or ions by the summation of the wave functions of all kinetic energy of atoms, the interaction with the external potential, and electron-electron potential interaction. Schrödinger equation is very complex and highly complicated for many atoms formation and leads to approximation using Hartree-Fock equation (HF) which is the first approach in ab-initio method [29]. Guided by semi-empirical method, Hartree-Fock method further simplify Schrödinger equation by using self consistent field method to approximate wave functions and the energies for atoms. By using consistent field method, Hartree-Fock method is neglecting electron correlation and leads to deviations from experimental results. To approach this weakness post Hartree-Fock method is devised and give rise to Møller-Plesset perturbation theory. Møller-Plesset perturbation theory improves Hartree-Fock method by introducing electron correlation effects by using perturbation theory from second up to fifth order (MP-n, $n=2, 3, 4, 5$). MP-n method is a standard level of theory in calculation involving a small fragment of a molecular system and usually requires high computational cost. Since MP-n method strictly follows the Schrödinger theory, the calculation is highly accurate. Anyhow, convergence using MP-n method can be slow and oscillatory depending on the chemical system and the basis set used. Hartree-Fock and all post Hartree-Fock methods can be considered as ab-initio method because they pursue the solutions imparted by Schrödinger equation [29,30].

Density Funtional Theory (DFT) is a quantum mechanical modeling method used to investigate the ground state electronic structure of many atoms or ions

system. With this theory many electron system can be determined using functionals not exactly from Schrödinger equation. Hence the name of DFT itself comes from the use of functionals of the electron density. DFT is the most popular and versatile methods available in computational physics or chemistry because it agrees satisfactorily with experimental data and is relatively involves low computational cost as compared to ab initio calculation.

The theory and concept of DFT roots to the two Hohenberg–Kohn theorems (H-K) [30]. The first H-K theorem shows that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial coordinates. It lays the groundwork for reducing the many-body problem of N number of electrons with $3N$ spatial coordinates to 3 spatial coordinates only through the use of functionals of the electron density. The second H-K theorem defines an energy functional for the whole system. Within the framework of Kohn-Sham, the intractable of many electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons including the exchange and correlation interactions. Modelling electron interactions is the difficult part in DFT. The simplest approximation is the local-density approximation (LDA), which is based on exact exchange energy for a uniform electron gas, that can be obtained from the Thomas–Fermi model and by numerical fitting to the correlation energy for a uniform electron gas. Thomas–Fermi model used a statistical model to approximate the distribution of electrons in an atom. The approximation in LDA is used where the functional depends only on the density at the coordinate where the functional is evaluated [29-31].

Another type of approximation is by using generalized gradient approximations (GGA). GGA is still based on LDA but also takes into account the gradient of the density at the same coordinate. GGA produces good results for molecular geometries and ground-state energies. Gradient correction to the LDA exchange functional was proposed in 1986 by Perdew and Wang (PW86) and was succeeded by PW91. Another correction was developed in 1988 by Becke (B88). Lee, Yang and Parr introduced a true gradient-based correlation functional through a numerical fit to the data of the helium atom and is abbreviated as LYP. Merging Becke's exchange correction to the LDA with the correlation functional of Lee, Yang and Parr resulted in a "BLYP" functional. This method gives rise to the highly successful hybrid DFT functional dubbed as B3LYP. Another GGA scheme by Perdew, Burke and Ernzerhof in 1996 (PBE) has become another standard and it is almost similar to PW91. A new class of GGA functional called HCTH was developed by Hamprecht, Cohen, Tozer and Handy in 1998. Such gradient-based functionals have addressed a serious LDA flaw when it comes to total-energy differences for example in magnetic materials. The various GGA approaches are similar with regard to the final results. The empirical knowledge about a particular system under study can provide some guidance in choosing the most suitable DFT functional [29,30,32].

2.3 Basis Set and Basis Set Superposition Error (BSSE)

Basis set is a mathematical representation of atomic orbital required in computational chemistry. When molecular calculations are performed, it is common to use a basis set composed of a finite number of atomic orbitals, centered at each

atomic nucleus within the molecule or a linear combination of atomic orbitals. Initially, these atomic orbitals were typically Slater orbitals, which correspond to a set of functions that decay exponentially with distance from the nuclei. Later, it was realized that these Slater-type orbitals could be approximated as linear combinations of Gaussian orbitals. It is easier to calculate overlap and other integrals with Gaussian basis functions and this leads to huge computational savings.

Today, there are hundreds of basis sets composed of Gaussian-type orbitals. The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The most common minimal basis set is STO- n G, where $n = 3, 4, 6$. This n value represents the number of Gaussian primitive functions that are included into a single basis function. In these basis sets, the core and valence orbitals contain the same number of Gaussian primitives. Minimal basis sets are fixed and are unable to adjust to different molecular environments. Minimal basis sets typically generate results that are insufficient for research-quality publication.

In molecular bonding, valence electrons are the ones that principally take part. Basis sets in which there are multiple basis functions corresponding to each valence atomic orbital are called valence double, triple, quadruple-zeta, and so on basis sets. They are also known as split-valence basis sets. The split-valence basis sets arise from the researchers at John Pople group is typically notated as $X\text{-}YZg$. X represents the number of primitive Gaussian functions in each core atomic orbital basis function. The Y and Z indicate for valence orbitals that are composed of two basis functions each, the first one is composed of a linear combination of Y primitive Gaussian functions, while the other is composed of a linear combination of Z primitive Gaussian functions. Split-valence triple- and quadruple-zeta basis sets are

denoted as $X\text{-}YZWg$ and $X\text{-}YZWVg$ respectively. The commonly used split-valence basis sets for this Pople type are 3-21G, 6-31G and 6-311G [34].

Some of the most widely used basis sets are those developed by Dunning and co-workers. They are designed to converge systematically to the complete-basis-set (CBS) limit using empirical extrapolation techniques. The basis sets are named as cc-pVNZ where N= D(Double), T(Triple), Q(Quadruple), etc. The 'cc-p', stands for 'correlation-consistent polarized' and the 'V' indicates they are valence-only basis sets. Other split-valence basis sets often have rather generic names such as TZVPP (Valence triple-zeta plus polarization) and QZVPP (Valence quadruple-zeta plus polarization).

The most common addition to minimal basis sets is probably the addition of polarization functions. For the basis sets developed by Pople's group, the addition of polarization function is denoted by an asterisk, *. Two asterisks, **, indicate that polarization functions are also added to light atoms (hydrogen and helium). When polarization is added to this basis set, a p-function is also added to the basis set. This adds some additional flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen nucleus. This is an important application when considering accurate representations of bonding between atoms, because the presence of the bonded atom makes the energetic environment of the electrons spherically asymmetric. Similarly, d-type functions can be added to a basis set with valence p orbitals, and f-functions to a basis set with d-type orbitals, and so on. A more precise notation indicates exactly which and how many functions are added to the basis set, such as (d,p) [33].

Another common addition to basis sets is the addition of diffuse functions, denoted in Pople-type sets by a plus sign, +, and in Dunning-type sets by "aug"

(from "augmented"). Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). These are very shallow Gaussian basis functions, which more accurately represent the "tail" portion of the atomic orbitals, which are further away from the atomic nuclei. These additional basis functions can be important when considering anions and other large, "soft" molecular systems [33].

In quantum chemistry, calculations of molecular properties are susceptible to basis set superposition error (BSSE) [29]. As the atoms of interacting molecules (or of different parts of the same molecule) approach one another, their basis functions overlap. Each monomer may "borrow" functions from other nearby components, effectively increasing its basis set and improving the calculation of energy. If the total energy is minimised as a function of the system geometry, the short-range energies from the mixed basis sets must be compared with the long-range energies from the unmixed sets, and this mismatch introduces an error. In counterpoise method (CP), BSSE is calculated by re-performing all calculations using the mixed basis sets, and the error is then subtracted from the uncorrected energy. The mixed basis sets are recognized by introducing "ghost orbitals" where the basis set functions have no electrons or protons associated with them.

2.4 Gaussian Software and Input File Configuration

Gaussian is a computational chemistry software program initially released in 1970 by John Pople and his research group at Carnegie-Mellon University as Gaussian 70. It has been continuously updated since then. The name originates from Pople's use of Gaussian orbitals to speed up calculations compared to those using Slater-type orbitals. The current version of the program is Gaussian 09. The